

IV.D.6 Development of High Temperature Membranes and Improved Cathode Catalysts

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Main Subcontractors:

High Temperature Membrane

Virginia Polytechnic Institute and State University (Virginia Tech), Blacksburg, Virginia

Pennsylvania State University, University Park, Pennsylvania

Stanford Research Institute International, Menlo Park, California

IONOMEM, Marlborough, Connecticut

Princeton University, Princeton, New Jersey

Cathode Catalysts

Northeastern University, Boston, Massachusetts

University of South Carolina, Columbia, South Carolina

United Technologies Research Center, East Hartford, Connecticut

Case Western Reserve University, Cleveland, Ohio

Objectives

- Develop and demonstrate an advanced polymeric membrane able to operate at near ambient (1-1.5 atmospheres) pressure in the temperature range of 120~150°C and able to meet DOE's program goals for performance.
- Develop and demonstrate improved high-concentration platinum (Pt) cathode catalysts that will enable the reduction of Pt loading to 0.05 milligrams per centimeter squared (mg/cm²) and meet DOE's goals for performance.

Approach

- Phase 1: High Temperature Membranes (HTMs) and improved Pt catalysts will be synthesized, characterized and compared with issued specifications.
- Phase 2: Laboratory-scale catalyst-coated membranes (CCMs) will be fabricated, optimized and tested using the Phase 1 down-selected membranes and catalysts.
- Phase 3: Full-size CCMs with the down-selected and optimized HTMs and catalysts will be fabricated and tested in two individual multi-cell stacks.

Accomplishments

- This project was initiated during the first quarter of 2002. Eight out of the nine subcontractors have initiated membrane and catalyst synthesis. Technical accomplishments for the four months since the initiation are given below.
- At Virginia Tech., high yields (>80%) of 3,3'-disulfonate, 4,4'-dichlorodiphenylsulfone were obtained by sulfonating commercially available monomers. Films (>40,000 molecular weight) drawn from these co-monomers showed negligible degradation in boiling water and acceptable proton conductivity at room temperature in water.
- United Technologies Corporation Fuel Cells (UTCFC) has developed and applied a new and novel in-situ electrochemical technique to quantify hydrogen crossover in membranes.
- High-concentration (40 weight percent [wt%]) ternary Pt alloy samples prepared using the carbothermal technique have yielded surface area and activity values comparable to commercial Pt samples. Platinum/Carbon (Pt/C) prepared by pulse-electrodeposition showed superior surface area and activity when compared to direct current deposited Pt/C electrodes.

Future Directions

- Continue polymer synthesis and evaluation of the fabricated films per membrane screening specifications. Initiate the fabrication of initial promising candidates into CCMs.
- Continue evaluation of Pt catalysts being synthesized using the colloidal sol, carbothermal and the electrodeposition techniques and compare results against catalyst screening specifications. Debug rotating disk electrode technique.

Introduction

Two main challenges in the PEMFC arena are the reduction of cathode Pt loading and development of membranes that can operate over 120°C. Surmounting these two challenges will directly affect the cost, performance and the size of PEMFC stacks. On the HTM project, new polymeric materials with negligible thermal degradation and acceptable proton conductivity in the 120-150°C range are required. On the improved catalyst project, a combination of higher activity catalysts and thinner catalyst layers is required to achieve the aggressive DOE performance targets.

Approach

To develop HTMs, UTCFC has teamed with research groups that possess competencies in the fields of polymer chemistry and engineering. The subcontractors on the HTM project are investigating modified Nafion® and new non-Nafion® based membrane systems (see Table 1). The subcontractors on the improved catalyst project and their individual approaches are given in Table 2.

Table 1. High Temperature Membrane Program Approach

Group	Principal Investigator	Approach
IONOMEM	Mr. Leonard Bonille	Hygroscopic solid ion conductor (e.g., zirconium phosphate, etc.) filled Nafion®
Penn State University	Prof. Digby Macdonald	Sulfones and sulfoxides of aromatic PPBP and aliphatic PVA. Covalent sulfonic acid bonded PEEK, PBI and PPBP
Princeton University	Prof. Andrew Bocarsly	Layered sulfonated Polystyrene/Fluoropolymer system
Stanford Research Institute	Dr. Susanna Ventura	Sulfonated PEEK-PBI-PAN
Virginia Tech	Prof. James McGrath	Sulfonated Poly(arylene ether sulfone)

Results

This project was initiated during the first quarter of 2002. Since then, all the subcontractors have hired appropriate personnel and initiated membrane/catalyst synthesis. A majority of the required processes are in place, and eight of the nine

Table 2. Advanced Cathode Catalyst Program Approach

Group	Principal Investigator	Approach
North Eastern University (NEU)	Prof. Sanjeev Mukerjee	Micellar Pt nano cluster synthesis, colloidal sol synthesis of binary Pt alloys
University of South Carolina (USC)	Prof. Branko Popov	Pulse electro-deposition of Pt and Pt alloys on Carbon [Pt and Pt-X, X=Fe, Ni, Co, Mn, Cu]
UTC Fuel Cells	Dr. Shari Bugaj	Carbothermal synthesis of ternary Pt alloys [Pt-Ir-X and Pt-Rh-X, [X=Ni, Co and V]]
Case Western Reserve University (CWRU)	Prof. Al Anderson	Quantum chemical modeling of Pt alloys and ORR
UT Research Center (UTRC)	Dr. Ned Cipollini	Reproducible and stack size CCM fabrication

subcontractors have reported preliminary results. At Case Western, the catalyst modeling work will start in September 2002, when Dr. Jerome Roques will start as a post doctoral associate. Some of the preliminary results obtained during the past four months are presented here.

High Temperature Membranes

To measure the gas crossover in HTMs, UTCFC developed a new in-situ electrochemical test. The test involves oxidizing the hydrogen that is transported across the membrane and measuring the limiting currents. Typical crossover limiting currents for two membranes of different thicknesses are depicted in Figure 1.

At VirginiaTech, 3,3'-disulfonate, 4,4'-dichlorodiphenylsulfone co-monomers with varying degrees of sulfonation were prepared from commercially available monomers. Nuclear magnetic resonance (NMR) spectroscopy was conducted on selected polymeric films to investigate the level of sulfonation. The NMR results showed that the sulfonation levels could be quantified very accurately. The water uptake of bi-phenol sulfone (BPSH) films increased with an increase in the degree of sulfonation. The membrane samples drawn from BPSH40 with 20, 30 and 40 K molecular

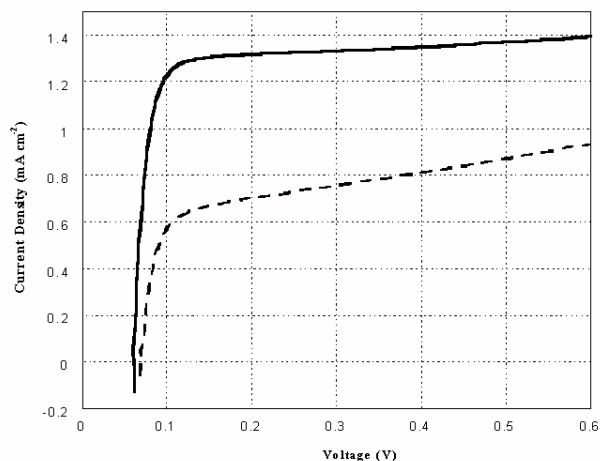


Figure 1. In-situ Limiting Hydrogen Crossover Currents for Two Membranes of Different Thicknesses

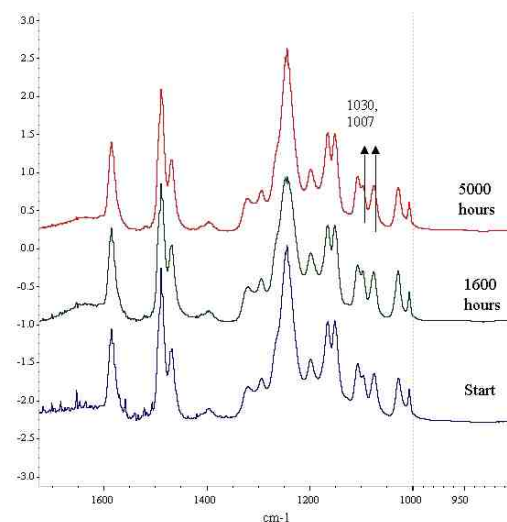


Figure 2. Influence of Hot Water Soxhlet Extraction on the FTIR of Sulfonated Poly(arylene ether) Copolymers BPSH40

weights showed proton conductivity values on the order of 0.09 S/cm. To evaluate the thermal degradation of the polymers, BPSH40 films were exposed to boiling water extractions using the Soxhlet technique in conjunction with Fourier transform infrared (FTIR) spectroscopy. The spectra were collected as a function of exposure time (see Figure 2). As seen from the figure, there is negligible change in the spectra up to 3,500 hours,

indicating that the hydrolytic stability of the films is excellent. No noticeable change in the nature or the ion exchange capacity of the membrane was noted during the Soxhlet experiment.

Penn State has modified electrochemical instrumentation that operates above 100°C. The accuracy of the instrumentation was confirmed by Nafion® 117 characterization. Princeton has initiated the synthesis of laminar membranes and anticipates initial characterization results on these materials over the next quarter. IONOMEM possesses a HTM that was shown to operate at 120°C prior to the start of this program. Since the initiation of this program, IONOMEM's efforts have been focused on electrode structure and catalyst modifications to establish a performance base.

Advanced Cathode Catalysts

UTCFC has modified the carbothermal synthesis process (U.S. Patent 4,677,092, US 4,806,515, US 5,013,618, US 4,880,711, US 4,373,014, etc.) to prepare 40 wt% ternary Pt alloy catalysts. Various high-concentration Pt catalyst systems were synthesized and the electrochemical surface area (ECA) and electrochemical activity values compared to commercially available catalysts (see Table 3). The UTCFC catalysts showed ECA and activity values comparable to the commercial catalysts. A rotating disk electrode technique for catalyst activity measurements has been developed and is currently being debugged at UTCFC.

Table 3. Preliminary ECA and Activity Data of Synthesized Pt Alloys

Catalysts	Catalysts ECA (m ² /Pt)	Catalyst Activity (A/gPt)
Commercial 50% Pt/C	98	25.1
Comercial 50% PTFE/C alloy	63	37.7
40% PT/Carbon C	110	27
40% Pt ₅₀ Ir ₂₃ Co ₂₅	75/62	33
40% Pt ₅₀ Ir ₂₃ Ni ₂₅	60	23

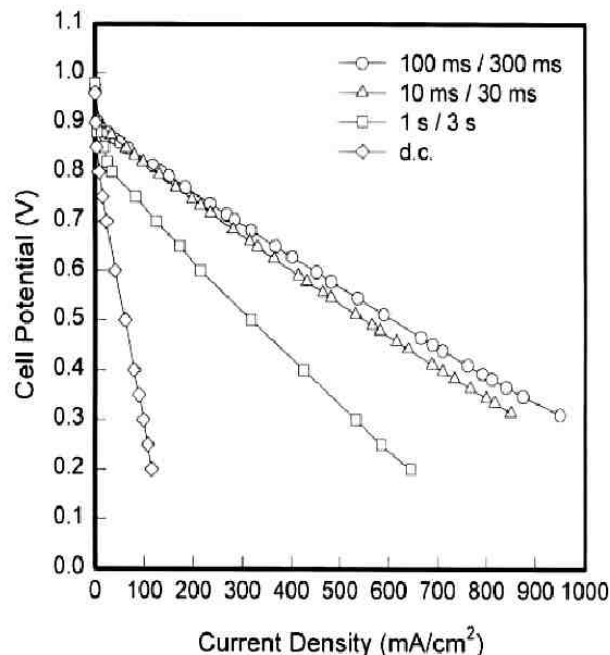


Figure 3. Polarization Curves at 50 milliamperes/cm² and Duty Cycle of 0.25

At the University of South Carolina, Pt/C electrodes were fabricated by using direct current (DC) and pulse current electrodeposition methods. With the use of current pulses rather than DC, a higher deposition current density could be used and Pt deposits with a higher surface area were possible. Figure 3 compares the polarization performance of electrodes prepared by pulse electrodeposition (current density=50 mA/cm² and duty cycle=0.25) and DC deposition. Electrodes fabricated under pulse deposition conditions display better performance than the DC-plated electrode. The best performance is obtained when the ON time is 100 ms and OFF time is 300 ms.

At NEU, a series of electrocatalysts were synthesized based on classical colloidal sol synthesis techniques. These included platinum nickel/carbon (PtNi/C), platinum chromium/carbon (PtCr/C), and platinum cobalt/carbon (PtCo/C) together with the control Pt/C. All of the above electrocatalysts were prepared with 20% metal loading on carbon support (Vulcan XC-72, Cabot Corp). Ohmic corrected Tafel

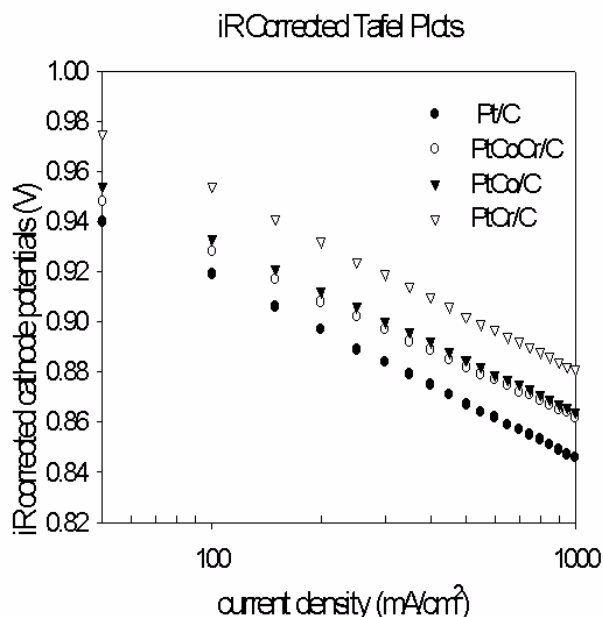


Figure 4. Ohmic Corrected Tafel Plots for Oxygen Reduction on Pt and Pt Alloy Electrocatalysts Prepared at Northeastern (note that PtCr/C is a system being considered only for ORR fundamentals; it will not be under consideration for down-selection)

plots for PtCr/C, PtCo/C, PtCoCr/C and PtNi/C are shown in Figure 4. As seen from the figure, the alloy catalysts are inherently more active than the Pt/C control. The data shows a lowering of the overpotential for oxygen reduction by up to 50 millivolts. At a potential of 0.9 volts, this translates to an eight-fold enhancement in oxidation-reduction reaction (ORR) activity. Stability and surface analysis of the Pt alloys was also performed using x-ray techniques.

Conclusions

The project is in its early stages and processes are in place for making progress. Preliminary results show that the HTM team is ramping up by initiating polymer synthesis processes and also by modifying instrumentation to perform high temperature measurements. On the advanced catalyst program, Pt and Pt alloys prepared using the colloidal sol, carbothermal and pulse electrodeposition processes are being characterized and compared with commercial Pt catalysts.

References

1. S. Kocha, P. Plasse, L. Onishi, D. Wheeler, J. Bett, AICHE Spring Meeting Proceedings- Fuel Cell Technology: Opportunities and Challenges, March 10-14, 2002, New Orleans.